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Gas sorption and transport in poly(tertiary-butyl methacrylate)

C. T. Wright and D. R. Paul*
Department of Chemical Engineering and Center for Polymer Research,
The University of Texas at Austin, Austin, TX 78712, USA

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Gas sorption and transport properties of poly(tertiary-butyl methacrylate) (PtBMA) have been measured at 35°C and are compared with prior results for poly(methyl acrylate) (PMA), poly(methyl methacrylate) (PMMA), and poly(ethyl methacrylate) (PEMA). The t-butyl substitution increases the gas permeability as a result of increases in both diffusivity and solubility coefficients; however, the ideal selectivity for a given gas pair may increase or decrease depending upon the methacrylate polymer to which it is compared. Poly(t-butyl methacrylate) does not show plasticization by CO_2 up to 10 atm of CO_2. The effect of t-butyl substitution on gas permeability observed here for the methacrylate polymer is compared to that reported in the literature for other polymer types. This substitution causes a larger increase in permeability the smaller the repeat unit of the base polymer since this results in a greater modification in structure and subsequent greater decrease in efficiency of chain packing.

(Keywords: poly(tertiary-butyl methacrylate); gases; sorption)

INTRODUCTION

Membrane technology has become competitive in both cost and performance in the gas separation industry. In many applications, membranes offer clear advantages over alternative technologies. To maintain an edge in these applications and expand to other areas, new generations of polymeric materials need to be identified that possess both higher productivity and selectivity. Research aimed at the development of improved membrane materials has typically involved the synthesis of new polymers, chemical modification of existing polymers, or chemical/physical modification of formed membranes. Common modification techniques include halogenation, sulfonation, and antiplasticization.

Our laboratory has most recently initiated a fundamental investigation of crosslinked gas separation membranes since this appears to be an attractive, but relatively unexplored, route for manipulating polymer free volume and its distribution to balance the selectivity *versus* permeability tradeoff. Most previous studies indicate that gas permeability of polymers is substantially reduced by crosslinking[1–16]. In fact, the rather low permeability of most crosslinked polymers has prevented them from being competitive membrane materials. However, recent research on polyimides has demonstrated that with appropriate tailoring of the polymer, crosslinking can be a useful modification technique[8,10,15]. The polyimides of interest had extremely high gas permeability coefficients before crosslinking as a result of a high free volume, and retained attractive levels of permeability after crosslinking.

The goal of the present work is to identify a high free volume, high permeability methacrylate-based polymer for use in a study of the effect of crosslinking on gas transport behaviour. Methacrylates offer a convenient method of synthesis, copolymerization, and crosslinking. Numerous methacrylate systems have been studied extensively and reported in the literature. They are quite well understood chemically and kinetically, which should facilitate characterization of a crosslinked membrane. Unfortunately, most methacrylate-type polymers have very low gas permeability coefficients, which is undesirable for our purposes.

However, by appropriate structural modifications, it should be possible to significantly increase the permeability of methacrylate-based polymers using recently established relationships between the chemical structure and transport properties of polymeric materials[17–33]. Structural changes that limit dense packing of polymer chain segments have been shown to increase permeability with little or no loss in permselectivity; e.g., addition of bulky pendant groups. Tertiary-butyl substitutions have been successfully used to inhibit chain packing and to substantially increase the gas permeability coefficients of polystyrene, polyarylates, and polyamides[21–24,26,34].

This paper examines the gas transport properties of poly(t-butyl methacrylate). The effects of the t-butyl group on gas permeation and sorption are explained in terms of changes in fractional free volume. Future papers will deal with how crosslinking of polymers based on t-butyl methacrylate alters permselectivity characteristics.

EXPERIMENTAL

Poly(t-butyl methacrylate) (PtBMA) was synthesized from t-butyl methacrylate monomer obtained from Monomer–Polymer and Dajac Laboratories. The monomer was washed three times with a 1M aqueous sodium

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* To whom correspondence should be addressed

hydroxide solution followed by a distilled water wash. The monomer was then dried over magnesium sulfate. After filtering to remove the magnesium sulfate, the monomer was placed in a small vial. About 1.7% methyl acrylate and 0.1% azobisisobutyronitrile, as received, were added to the vial. The solution was purged with nitrogen for 15 min and then polymerized in a water bath at 55°C for about 6 h. The contents were dissolved in tetrahydrofuran, precipitated three times into a 70/30 methanol/water mixture, and dried at 80°C in a convection oven overnight.

Dense films of PtBMA, 3–4 mil in thickness, were prepared by solution casting from chloroform on glass plates. A 5 μm Teflon filter was used to remove particulate contamination from the polymer solution. Casting was performed in a sealed glove bag to provide a solvent-saturated environment and slow evaporation. After the solvent had evaporated, the films were dried in a vacuum oven by incrementally increasing the temperature to above the glass transition temperature and holding it there for two days. The films were then air quenched to room temperature. Thermogravimetric analysis was used to ensure that removal of the solvent was complete.

A Perkin-Elmer differential scanning calorimeter was used to measure the glass transition temperature, T_g, of the polymers at a heating rate of 20°C min^{-1}. The T_g was taken as the onset of the heat capacity step change during the second scan. A density gradient column filled with an aqueous calcium nitrate solution was used to determine the polymer density at 30°C. The density was used to calculate the fractional free volume (FFV) from

$$\mathrm{FFV} = \frac{V - V_0}{V} \tag{1}$$

where V is the specific volume and V_0 is the occupied volume of the polymer. The occupied volume was calculated from the van der Waals volume by the method of Bondi[35]

$$V_0 = 1.3\,\mathrm{V_w} \tag{2}$$

The van der Waals volumes estimated by a group contribution method are 86.8 cm^3 mol^{-1} for PtBMA, 45.9 cm^3 mol^{-1} for poly(methyl acrylate) (PMA), 56.1 cm^3 mol^{-1} for poly(methyl methacrylate) (PMMA), and 66.3 cm^3 mol^{-1} for poly(ethyl methacrylate) (PEMA)[36].

The molecular weight of PtBMA was measured with a gel permeation chromatograph calibrated with polystyrene standards. The PtBMA films prepared here were quite brittle. The high molecular weight of the PtBMA indicates that this brittleness is inherent in the material and not the result of a low molecular weight product.

A pressure-rise permeation cell, described previously, was used to measure the pure gas permeability coefficients for the polymer films to He, H_2, O_2, N_2, CH_4, and CO_2[37]. Because of the brittleness of the films, the upstream driving pressure was not raised above 10 atm. CO_2 permeation was measured last to avoid any conditioning effects[38]. A dual-volume pressure-decay sorption cell was used to measure the sorption isotherms for N_2, CH_4, and CO_2 up to 30 atm[37,39].

The ideal selectivity was calculated from the ratio of permeabilities

$$\alpha_{\mathrm{A/B}} = \frac{P_{\mathrm{A}}}{P_{\mathrm{B}}} \tag{3}$$

where P_{A} and P_{B} are the permeabilities of pure gases A and B. The ideal selectivity is usually a good estimate of actual mixed gas selectivity in the absence of penetrant–penetrant interactions, competitive sorption, and plasticization[40,41].

RESULTS AND DISCUSSION

Polymer characterization

The physical properties of PtBMA are shown in *Table 1* along with those of PMA, PMMA and PEMA which are included for comparative purposes[42–44]. The t-butyl substitution results in a 13°C, 50°C and 101°C increase in T_g compared to PMMA, PEMA and PMA, respectively. The elevation in T_g results from the significant hindrance of large-scale motions of the polymer backbone caused by the t-butyl group. The α-methyl group on the methacrylate materials, however, appears to be even more effective for hindering chain motion. This substitution results in an 88°C increase in T_g from PMA to PMMA. Krause *et al.*[45] attribute this dramatic effect to the fact that the α-methyl group introduces bulk without flexibility directly next to the polymer backbone. The t-butyl group similarly adds bulk to the polymer chain without flexibility but is more remote from the backbone. At the temperatures used in this study, PtBMA, PMMA and PEMA are in the glassy state while PMA is in the rubbery state.

PtBMA has the highest FFV of the polymers shown in *Table 1* and is comparable to aromatic polymers with very rigid packing disruptive groups[21]. The FFV of the methacrylates increases as the size of the side group increases, i.e. PtBMA > PEMA > PMMA. The side group disrupts chain packing, and the effect is greater the bulkier the side group. Addition of the α-methyl group, however, causes a 16% decrease in FFV (compare PMA to PMMA) due to more efficient packing.

Table 1 Physical properties of selected acrylic polymers

Polymer	Acronym	Source	Density (g cm^{-3})	Molecular weight[a] $\bar{M}_w$	T_g (°C)	Fractional free volume
Poly(t-butyl methacrylate)	PtBMA	synthesized here	1.023	375 800	119	0.188
Poly(methyl acrylate)[b]	PMA	Celanese Chemical Co	1.211	576 000	18	0.161
Poly(methyl methacrylate)[c]	PMMA	Rohm & Haas Plexiglas V(811)	1.188	105 400	106	0.135
Poly(ethyl methacrylate)[d]	PEMA	DuPont Elvacite 2042	1.124	438 000	69	0.151

[a] Intrinsic viscosity of PtBMA measured in $CHCl_3$ at 25°C is 1.44 dl g^{-1}
[b] Data from ref. 43
[c] Data from ref. 42
[d] Data from ref. 44

Gas permeation

Pure gas permeability coefficients for PtBMA are shown in *Figure 1* as a function of upstream driving pressure. The permeability coefficients for all gases are essentially independent of upstream driving pressure. This trend was also seen with PMA, PMMA and PEMA for all gases, except for CO_2 whose permeability coefficient increases with upstream pressure due to plasticization of these polymers by sorbed CO_2[42–44]. No plasticization was observed for PtBMA up to 10 atm CO_2. In the absence of plasticization, gas permeability coefficients generally decrease slightly with upstream pressure for glassy polymers; this is often explained in terms of the dual sorption model, using the assumption of partial immobilization. In terms of this model, the current results would suggest complete immobilization[46].

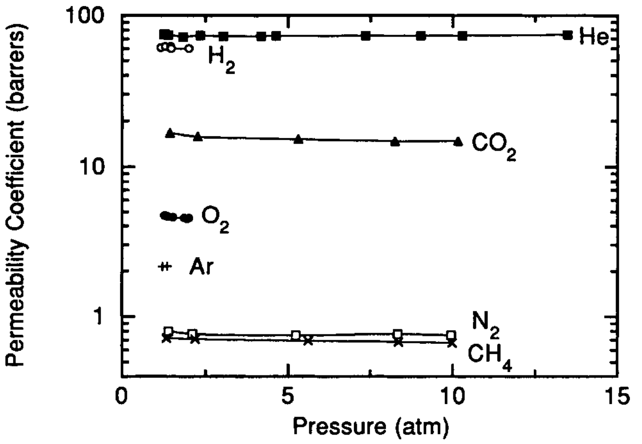


Figure 1 Effect of pressure on the gas permeability coefficients of PtBMA at 35°C

Table 2 Helium permselectivity characteristics of acrylic polymers at 35°C and 2 atm

Polymer	P_{He} (barrers)	α_{He/CH_4}	α_{He/H_2}
PtBMA	74.6	104	1.20
PMA[a]	10.6	45.1	—
PMMA[b]	8.05	1390	2.01
PEMA[c]	23.8	68.6	1.09

[a] Data from ref. 43
[b] Data from ref. 42
[c] Data from ref. 44

It is instructive to compare the gas transport properties of PtBMA to those of other methacrylates and acrylates; see *Tables 2–4*. Obviously, the gas permeability and ideal selectivity are dependent on many factors such as size and location of substituents and on whether the polymer is in the glassy or the rubbery state. The O_2 and N_2 results for PtBMA are of particular interest. PtBMA is about 50 times more permeable to O_2 than PMMA but its O_2/N_2 selectivity is somewhat less; PtBMA is more permeable to O_2 than PEMA, with a slightly higher O_2/N_2 selectivity. The CO_2 permeability of PtBMA is larger than that of PMMA by a factor of about 40, but its ideal selectivity for CO_2/CH_4 is much less than that of PMMA; however, due to plasticization by CO_2, the high ideal selectivity of PMMA is not realized in actual CO_2/CH_4 mixtures at high CO_2 partial pressures[41].

Previous studies have shown that an approximate correlation exists between gas permeability, P, and polymer fractional free volume, FFV, of the form

$$P = A\exp\left(\frac{-B}{\mathrm{FFV}}\right) \qquad (4)$$

where A and B are parameters independent of polymer type. Values of the parameters A and B can be calculated from the correlations published in each of these studies. *Figures 2* and *3* show plots of this type for O_2 and CO_2.

Table 3 O_2/N_2 permselectivity characteristics of acrylic polymers at 35°C and 2 atm

Polymer	P_{O_2} (barrers)	α_{O_2/N_2}	$\bar{S}_{O_2}$[a] (cm^3(STP)cm^{-3}atm^{-1})	$\bar{S}_{O_2}/\bar{S}_{N_2}$	$\bar{D}_{O_2} \times 10^8$[b] (cm^2 s^{-1})	$\bar{D}_{O_2}/\bar{D}_{N_2}$
PtBMA	4.53	5.90	0.32	1.5	10.8	3.93
PMA[c]	—	—	—	—	—	—
PMMA[d]	0.096	7.13	0.19	1.5	0.39	4.67
PEMA[e]	1.86	5.71	0.12	1.8	11.5	3.17

[a] Calculated from $S = P/D$
[b] Calculated from time-lag measurements
[c] Data not available
[d] Data from ref. 42
[e] Data from ref. 44

Table 4 CO_2/CH_4 permselectivity characteristics of acrylic polymers at 35°C and 1 atm

Polymer	P_{CO_2} (barrers)	α_{CO_2/CH_4}	$\bar{S}_{CO_2}$[a] (cm^3(STP)cm^{-3}atm^{-1})	$\bar{S}_{CO_2}/\bar{S}_{CH_4}$	$\bar{D}_{CO_2} \times 10^8$[b] (cm^2 s^{-1})	$\bar{D}_{CO_2}/\bar{D}_{CH_4}$
PtBMA	15.1	21.0	2.90	4.17	3.95	5.01
PMA[c]	6.77	28.8	1.98	13.4	2.60	2.15
PMMA[d]	0.36	61.6	3.44	8.76	0.079	6.96
PEMA[e]	7.01	20.2	1.48	9.26	3.59	2.25

[a] Calculated from the sorption isotherm
[b] Calculated from $D = P/S$
[c] Data from ref. 43
[d] Data from ref. 42
[e] Data from ref. 44

The dashed lines represent the best fit to data for a wide range of polysulfone materials[27–31]. The data for the acrylic polymers agree rather well with the polysulfone results. However, there may be other issues that affect permeability that are not accounted for by FFV.

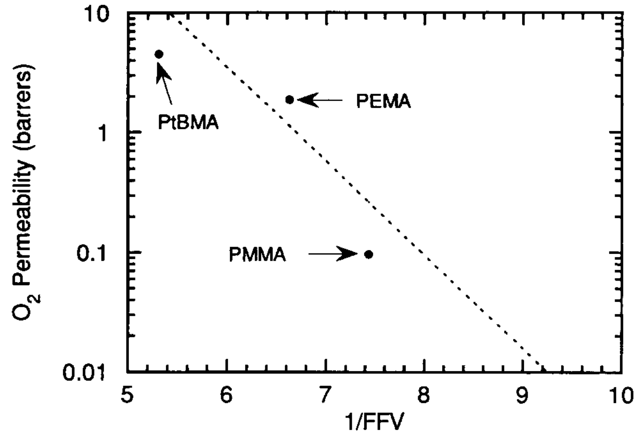


Figure 2 Correlation of oxygen permeability with fractional free volume for acrylic polymers at 2 atm and 35°C. The dotted line represents data for various polysulfones[27–31]

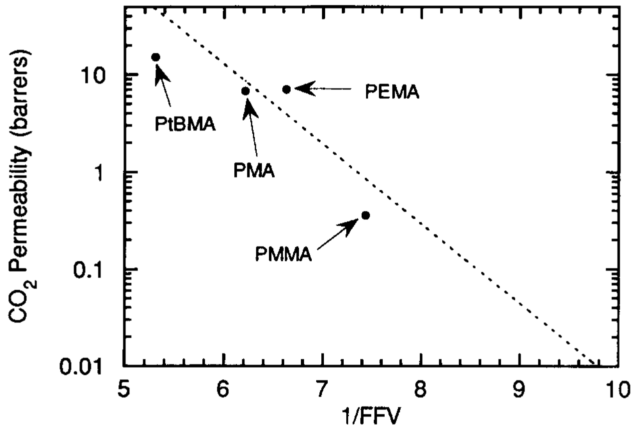


Figure 3 Correlation of carbon dioxide permeability with fractional free volume for acrylic polymers at 1 atm and 35°C. The dotted line represents data for various polysulfones[27–31]

Gas sorption

Pure gas sorption isotherms for N_2, CH_4 and CO_2 are given in *Figure 4* for PtBMA. As expected, the more condensable gases exhibit higher levels of solubility; CO_2 sorption is highest and N_2 is lowest. The isotherms are concave to the pressure axis and are well described by the dual mode sorption model

$$C = k_{D}p + \frac{C'_{H}bp}{1+bp} \tag{5}$$

where k_d is the Henry's law coefficient, C'_H is the Langmuir capacity constant, and b is an affinity parameter. The parameters given in *Table 5* were calculated by a non-linear least squares fit of the data to equation (5) and provide a compact method of describing the sorption isotherms. The correlation coefficients in *Table 5* demonstrate that these parameters provide a good representation of the data. The actual certainty of these sorption parameters, however, depends on the curvature of the isotherms. When this curvature is weak, estimation of $C'_H b$ is more accurate than that of C'_H and b individually[47]. Since PMA is in the rubbery state, it shows a linear isotherm, i.e. Henry's law, rather than the non-linear form of the dual mode sorption model. The parameters

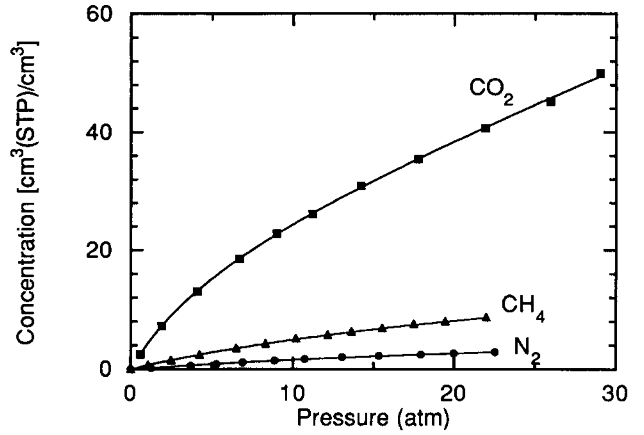


Figure 4 Sorption isotherms for nitrogen, methane and carbon dioxide in PtBMA at 35°C. The sample was conditioned at 30 atm of CO_2 for 48 h prior to CO_2 measurements

Table 5 Gas sorption parameters for acrylic polymers at 35°C

Polymer	Gas	k_D ($cm^3(STP)cm^{-3}atm^{-1}$)	C'_H ($cm^3(STP)cm^{-3}$)	b (atm^{-1})	Correlation coefficient
PtBMA	N_2	0.0259	6.00	0.029	0.9979
	CH_4	0.132	11.1	0.049	0.9992
	CO_2[a]	1.09	21.7	0.163	0.9999
PMA[b]	N_2	0.037	—	—	
	CH_4	0.147	—	—	
	CO_2	1.98	—	—	
PMMA[c]	N_2	—	—	—	
	CH_4	0.199	1.53	0.153	
	CO_2[d]	1.20	15.6	0.172	
PEMA[e]	N_2	—	—	—	
	CH_4	0.165	2.24	0.054	
	CO_2	1.48	11.9	0.071	

[a] Prior to these measurements, the sample was conditioned at 30 atm of CO_2 for 48 h
[b] Data from ref. 43
[c] Data from ref. 42
[d] Prior to these measurements, the sample was conditioned at 25 atm of CO_2 for 24 h
[e] Data from ref. 44

k_d, C'_H and b are lowest for N_2 and highest for CO_2. Since each of the methacrylates has a different CO_2 history, it is difficult to make comparisons based on these data alone. From the CH_4 data, it appears that the t-butyl substitution results in a substantial increase in the Langmuir capacity term, C'_H, which is consistent with the change in free volume, and a small decrease in the Henry's law constant, k_d.

The effect of t-butyl substitution on gas sorption can be related in part to changes in fractional free volume. When all other factors are the same, an increase in free volume leads to a higher level of gas sorption. *Figures 5* and *6* show a correlation between gas solubility and FFV for O_2 and CO_2. The dashed lines were constructed to represent boundaries that include all data for a number of polysulfones (open circles), as described elsewhere[27–31]. The open squares represent data for a number of polyarylates, described elsewhere, which generally follow the trend defined by the polysulfone results[21]. The closed points show results for the current acrylic polymers. For O_2, PMMA falls within the solubility band given by the dotted lines while PtBMA and PEMA fall below this band. For CO_2, PMMA lies above the band, PMA and PEMA lie within the band, while PtBMA lies just below the band. The differences in gas solubility for PMMA, PEMA and PtBMA can be related to the density of carbonyl groups in these materials. A correlation between the concentration of carbonyl groups and the solubility of CO_2 (relative to that of CH_4) has been noted by previous researchers[48]; a similar correlation is shown in *Figure 7*. The t-butyl substitution reduces the carbonyl concentration within the polymer, which tends to reduce the CO_2/CH_4 solubility selectivity. The high concentration of carbonyl groups in PMMA increases the frequency of polar interactions with CO_2 and enhances its solubility in this polymer. Although PMA has the highest carbonyl density of these acrylic polymers, it does not exhibit the highest absolute level of CO_2 solubility. PMMA is in the glassy state while PMA is in the rubbery state; because of the resulting differences in volumetric characteristics, the gas solubility in PMMA is considerably higher than that in PMA.

The gas permeability coefficient can be factored into solubility and diffusivity terms as suggested by

$$P = D \cdot S \tag{6}$$

The solubility coefficient, S, can be calculated from the secant slope of the sorption isotherm evaluated at the appropriate upstream pressure. The diffusivity is then calculated from the ratio of permeability and solubility. Alternately, an apparent diffusion coefficient can be calculated from

$$D = \frac{\ell^2}{6\Theta} \tag{7}$$

where ℓ is the film thickness and Θ is the diffusion time lag; an apparent solubility coefficient can then be calculated from equation (6). The CO_2/CH_4 (*Table 4*) results were calculated by the former method; the O_2/N_2 (*Table 3*) results by the latter. The ideal selectivity can also be factored into solubility and diffusivity ratios as follows:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B}\right) \cdot \left(\frac{S_A}{S_B}\right) \tag{8}$$

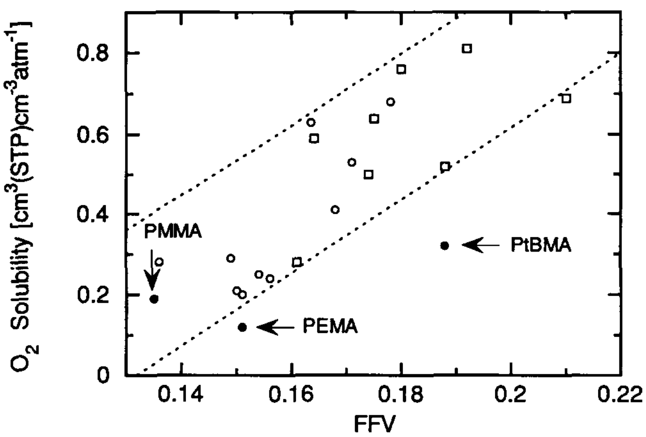


Figure 5 Correlation of oxygen solubility coefficient at 2 atm and 35°C with fractional free volume for acrylic polymers (●), polyarylates[21] (□) and polysulfones[27–31] (○). The dotted lines represent suggested boundaries of the data for the various polysulfones[27–31]

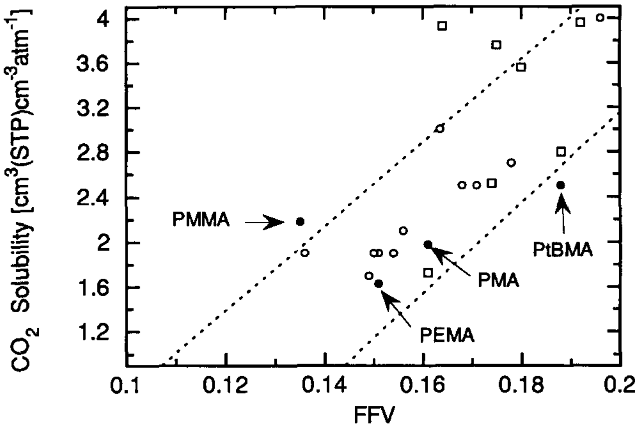


Figure 6 Correlation of carbon dioxide solubility coefficient at 10 atm and 35°C with fractional free volume for acrylic polymers (●), polyarylates[21] (□) and polysulfones[27–31] (○). The dotted lines represent suggested boundaries of the data for the varous polysulfones[27–31]

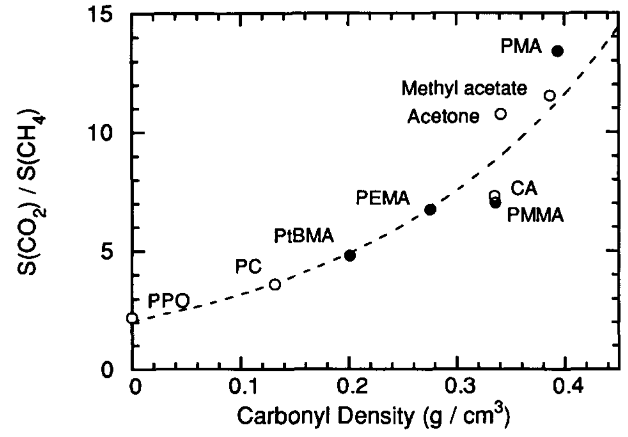
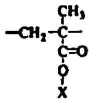
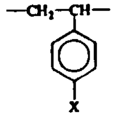
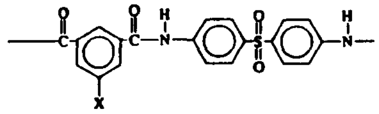
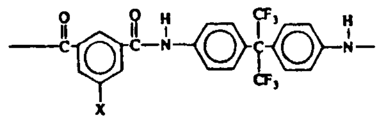
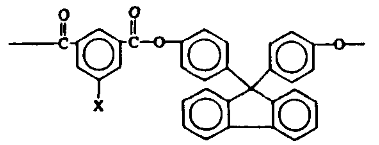
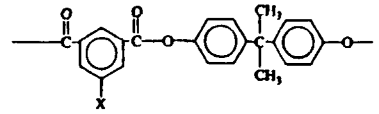


Figure 7 Correlation of CO_2/CH_4 solubility selectivity at 20 atm and 35°C with carbonyl density. Solid circles represent data for the acrylic polymers. For reference, data from the literature[47] for poly(phenylene oxide), PPO; polycarbonate, PC; cellulose acetate, CA; acetone; and methyl acetate are shown as open circles. The dotted line represents the best exponential fit of the data

The diffusion and solubility coefficients are shown in *Tables 3* and *4*. PtBMA has larger diffusion coefficients than PMMA and PMA for all gases. PtBMA has larger diffusion coefficients than PEMA for the fast gases such

Table 6 Structures and properties of t-butyl substituted polymers

		Base polymer			t-Butyl substituted polymer		
Acronym	Polymer repeat unit	X=	Molar volume of repeat unit (cm^3 mol^{-1})	P_{O_2} (barrers)	X=	Molar volume of repeat unit (cm^3 mol^{-1})	P_{O_2} (barrers)
MMA		-CH$_3$	84.3	0.096	-C(CH$_3$)$_3$	139	4.53
PS[a]		-H	99.2	2.9	-C(CH$_3$)$_3$	169	35.5
IP/SO$_2$[b]		-H	274	0.19	-C(CH$_3$)$_3$	342	2.0
IP/6F[b]		-H	329	2.4	-C(CH$_3$)$_3$	399	11.5
FBP[c]		-H	393	3.03	-C(CH$_3$)$_3$	468	9.55
BPA[c]		-H	296	1.33	-C(CH$_3$)$_3$	368	5.95

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[a] Permeability coefficient reported at 1 atm (data from ref. 26)
[b] Permeability coefficient reported at 10 atm (data from ref. 34)
[c] Permeability coefficient reported at 2 atm (data from ref. 21)

as CO_2 but lower diffusion coefficients for the slower gases such as O_2, N_2 and CH_4. The solubility coefficients for PtBMA are larger than those for PMMA, PMA and PEMA for all gases except CO_2. A comparison of the O_2/N_2 permeation results for PtBMA and PEMA shows that both polymers have similar selectivities and diffusivities. The larger permeability for PtBMA than for PEMA is caused by an increase in solubility. It is surprising that the diffusivities of PEMA and PtBMA are about the same whereas the sizes of the side groups are quite different.

Comparison with t-butyl substitution in other polymers

The effects of the tertiary-butyl group on gas permselectivity characteristics have been examined for several other polymer types, viz. polystyrene, polyarylates and polyamides[21-24,26,34]. The structures and properties of these polymers, plus those of the current methacrylate materials, are shown in *Table 6*. Plots of O_2/N_2 ideal selectivity *versus* O_2 permeability for these materials are shown in *Figure 8*. The base polymers (X = a hydrogen or methyl group) are shown as open symbols while the t-butyl substituted materials are shown as closed symbols. The solid line represents an 'upper bound' proposed by Robeson above which no polymers are currently known to exist[49]. In each case, t-butyl substitution results in an increase in O_2 permeability and a loss in O_2/N_2 selectivity. The pressures at which the permeability results are reported for the various polymers are not the same. Since pressure can affect permeability, there may be a variability that should be kept in mind in making comparisons.

It is apparent from *Figure 8* that the magnitude of the permeability change resulting from the t-butyl substitution is quite different for the various polymers. These differences can be understood in terms of the relative size of the polymer repeat units. The permeability of the t-butyl substituted material relative to that of the base polymer decreases as the molar volume of the repeat unit of the base polymer increases, as shown in *Figure 9*. This trend results from the fact that when the polymer repeat unit is large, substitution of a t-butyl group represents a smaller relative change in structure (hence, chain packing or permeability) than when the repeat unit is small. Since PMMA has the smallest repeat unit of the polymers considered, the consequence of t-butyl substitution is quite large. It is important to note that in all of the comparisons made in *Table 6* the t-butyl group is substituted for a hydrogen except in the methacrylate case where it replaces a methyl group. If the t-butyl group were replacing a hydrogen in the methacrylate material, the relative change in gas permeability coefficient might be even greater.

CONCLUSIONS

Gas sorption and transport properties of poly(t-butyl methacrylate) are reported here and compared to those of other methacrylate and acrylate polymers. Increasing the size of the alkyl side group increases the permeability of all gases as expected and the t-butyl group is especially effective for this purpose. This permeability increase results from increases in both the diffusion and solubility coefficients, primarily due to the increase in free volume, or reduced efficiency of chain packing, due to the large, bulky character of the t-butyl group. In addition, substitution of smaller alkyl units by the t-butyl group dilutes the concentration of carbonyl groups within acrylic polymers. Carbonyl groups give rise to polar interactions with CO_2 and typically enhance CO_2 solubility and permeability.

Previous work has shown that incorporation of t-butyl groups increases the gas permeability of a number of different polymer types. It is shown here that the extent of the increase in permeability caused by t-butyl substitution depends strongly on the size of the repeat unit of the base polymer. This substitution causes a

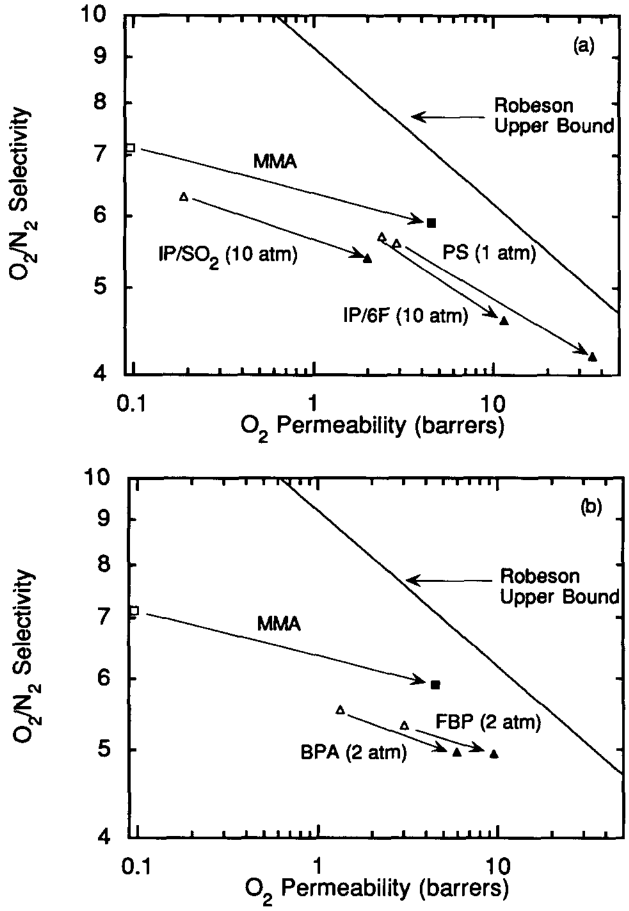

Figure 8 Comparison of the effect of t-butyl substitution on oxygen/nitrogen permselectivity characteristics for poly(methyl methacrylate) with polyamides and polystyrene (a) and with polyarylates (b). All data at 35°C

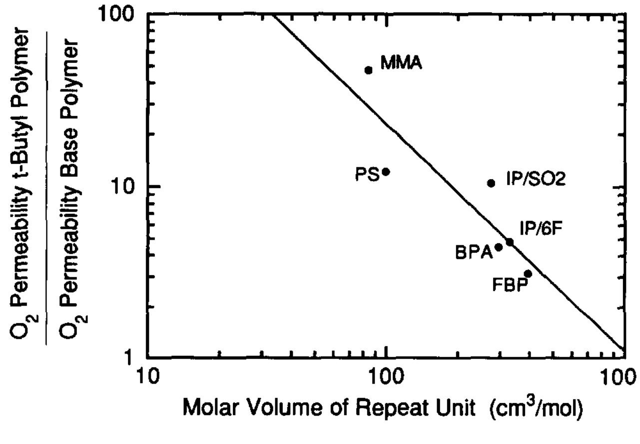

Figure 9 Effect of molar volume of the base polymer repeat unit on the ratio of the O_2 permeability coefficient of the t-butyl substituted polymer to that of the original base polymer

larger structural modification and reduction in chain packing efficiency, and hence a greater increase in permeability, the smaller the original repeat unit. Since PMMA has a small repeat unit compared to the other polymers considered to date, it shows the greatest enhancement in permeability.

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